

THAT WHICH IS CLAIMED:

sup

1. A process of forming a resist image in a microelectronic substrate, said process comprising the steps of:

5 contacting the substrate with a composition first comprising carbon dioxide and a component selected from the group consisting of at least one polymeric precursor, at least one monomer, at least one polymeric material, and mixtures thereof, to deposit the component on the substrate and form a coating thereon; then

10 imagewise exposing the coating to radiation such that exposed and unexposed coating portions are formed; and then

subjecting the coating to a second composition comprising carbon dioxide having such that either one of the exposed or the unexposed coating portions are removed from the substrate and the other coating portion is developed and remains on the coating to form an image thereon.

15

2. The process according to Claim 1, wherein the exposed coating portion has a lower solubility in carbon dioxide relative to the unexposed coating portions, and wherein said step of subjecting the coating to a second composition comprising carbon dioxide comprises removing the unexposed coating portion from the substrate such that the exposed developed coating portion remains.

20

3. The process according to Claim 2, wherein the polymeric material comprises a fluoropolymer.

25

4. The process according to Claim 3, wherein the fluoropolymer is formed from monomers selected from the group consisting of fluoroacrylate monomers, fluorostyrene monomers, fluoroalkylene oxide monomers, fluorolefin monomers, fluorinated alkyl vinyl ether monomers, cyclic fluorinated monomers, and mixtures thereof.

30

5. The process according to Claim 4, wherein the monomers are selected from the group consisting of 2-(N-ethylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-ethylperfluorooctane- sulfonamido) ethyl methacrylate, 2-(N-methylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-methylperfluorooctane- sulfonamido) ethyl methacrylate, 1,1'-dihydroperfluorooctyl acrylate, 1,1'-dihydroperfluorooctyl methacrylate, 1,1',2,2'-tetrahydroperfluoroalkylacrylate, 1,1',2,2'-tetrahydroperfluoroalkyl-methacrylate, α -fluorostyrene, 2,4,6-trifluoromethylstyrene, hexafluoropropylene oxide, perfluorocyclohexane oxide, tetrafluoroethylene, vinylidene fluoride, chlorotrifluoroethylene, perfluoro(propyl vinyl ether), perfluoro(methyl vinyl ether), 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole, and mixtures thereof.

6. The process according to Claim 2, wherein the polymeric material comprises a silicon-containing polymer.

7. The process according to Claim 6, wherein the silicon-containing polymer comprises at least one segment selected from the group consisting of an alkyl siloxane, a fluoroalkyl siloxane, a chloroalkyl siloxane, and mixtures thereof.

8. The process according to Claim 2, wherein an intermediate layer is present between the coating portion and the substrate, and said process further comprising the step of selectively etching the intermediate layer using the developed coating portion as an etching mask.

9. The process according to Claim 8, wherein said step of selectively etching the intermediate layer comprises contacting the intermediate layer with a gas selected from the group consisting of oxygen, chlorine, fluorine, and mixtures thereof.

10. The process according to Claim 2, further comprising the steps of:

depositing a metal-containing material or an ionic material on the surface of the substrate from which the exposed or the unexposed coating

5 portions were removed; and then

removing the exposed coating portion from the substrate.

11. The process according to Claim 10, wherein the metal-containing material comprises at least one metal selected from the group consisting of aluminum, copper, gold, titanium, tantalum, tungsten,
10 molybdenum, silver, and alloys thereof.

12. The process according to Claim 10, wherein the ionic material is selected from the group consisting of boron, phosphorous, arsenic, and
15 combinations thereof.

13. The process according to Claim 2, wherein the radiation is selected from the group consisting of visible, ultraviolet, x-ray, and e-beam.

14. The process according to Claim 13, wherein the radiation is ultraviolet or x-ray and the composition comprising polymeric material includes a photo acid generator.
20

15. The process according to Claim 10, wherein said step of removing the exposed coating portion from the substrate comprises contacting the exposed coating portion with a carbon dioxide containing fluid such that the exposed coating portion is removed from the substrate.
25

16. The process according to Claim 2, wherein said step of contacting the substrate with a first composition comprising carbon dioxide and a component comprises coating the component using a method selected from the group consisting of a spin coating method, a dip coating method, a
30

meniscus coating method, a coating method using self-assembled monolayers, and a spray coating method.

17. The process according to Claim 2, wherein the polymeric
5 material is a copolymer of 1,1'-dihydroperfluorooctyl methacrylate and t-butyl methacrylate.

18. The process according to Claim 1, wherein the exposed coating
portion has a higher solubility in carbon dioxide relative to the unexposed
10 coating portion, and wherein said step of subjecting the coating to a second composition comprising carbon dioxide comprises removing the exposed coating portion from the substrate such that the unexposed coating portion remains.

19. The process according to Claim 18, wherein the polymeric
15 material comprises a fluoropolymer.

20. The process according to Claim 19, wherein the fluoropolymer
is formed from monomers selected from the group consisting of fluoroacrylate
20 monomers, fluorostyrene monomers, fluoroalkylene oxide monomers, fluorolefin monomers, fluorinated alkyl vinyl ether monomers, cyclic fluorinated monomers, and mixtures thereof.

21. The process according to Claim 20, wherein the monomers are
25 selected from the group consisting of 2-(N-ethylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-ethylperfluorooctane- sulfonamido) ethyl methacrylate, 2-(N-methylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-methylperfluorooctane- sulfonamido) ethyl methacrylate, 1,1'-dihydroperfluorooctyl acrylate, 1,1'-dihydroperfluorooctyl methacrylate,
30 1,1',2,2'-tetrahydroperfluoroalkylacrylate, 1,1',2,2'-tetrahydroperfluoroalkyl-methacrylate, α -fluorostyrene, 2,4,6-trifluoromethylstyrene, hexafluoropropylene oxide, perfluorocyclohexane oxide, tetrafluoroethylene,

vinylidene fluoride, chlorotrifluoroethylene, perfluoro(propyl vinyl ether), perfluoro(methyl vinyl ether), 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole, and mixtures thereof.

5 22. The process according to Claim 18, wherein the polymeric material comprises a silicon-containing polymer.

10 23. The process according to Claim 22, wherein the silicon-containing polymer comprises at least one segment selected from the group consisting of an alkyl siloxane, a fluoroalkyl siloxane, a chloroalkyl siloxane, and mixtures thereof.

15 24. The process according to Claim 18, wherein an intermediate layer is present between the coating portion and the substrate, and said process further comprising the step of selectively etching the intermediate layer using the developed coating portion as an etching mask.

20 25. The process according to Claim 24, wherein said step of selectively etching the intermediate layer comprises contacting the intermediate layer with a gas selected from the group consisting of oxygen, chlorine, fluorine, and mixtures thereof.

25 26. The process according to Claim 18, further comprising the steps of:
deposited a metal-containing material or an ionic material on the surface of the substrate from which the exposed or the unexposed coating portions were removed; and then
removing the exposed coating portion from the substrate.

30 27. The process according to Claim 26, wherein the metal-containing material comprises at least one metal selected from the group

consisting of aluminum, copper, gold, titanium, tantalum, tungsten, molybdenum, silver, and alloys thereof.

28. The process according to Claim 27, wherein the ionic material is
5 selected from the group consisting of boron, phosphorous, arsenic, and combinations thereof.

29. The process according to Claim 18, wherein radiation is
10 selected from the group consisting of visible, ultraviolet, X-ray, and e-beam.

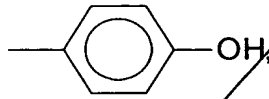
30. The process according to Claim 18, wherein the radiation is
ultraviolet or x-ray and the first composition comprises a photo acid generator.

31. The process according to Claim 18, wherein said step of
15 removing the unexposed coating portion from the substrate comprises contacting the unexposed coating portion with a carbon dioxide containing fluid such that the unexposed coating portion is removed from the substrate.

32. The process according to Claim 18, wherein said step of
20 contacting the substrate with a first composition comprising carbon dioxide and a component comprises coating the component using a method selected from the group consisting of a spin coating method, a dip coating method, a meniscus coating method, a coating method using self-assembled monolayers, and a spray coating method.

33. The process according to Claim 18, wherein the component
25 includes a polymeric material is selected from the group consisting of a copolymer of a fluoroacrylate and a component selected from the group consisting of $C(CH_2OH)_3$, a sugar unit, and SiR_3 wherein R is a polar group
30 selected from the group consisting of:

—CH₂CH₂CH₂OH,



—CH₂CH₂CH₂-C≡N, and

mixtures thereof.

34. A process of forming integrated circuits comprising the steps of:

5 (a) contacting at least one wafer with a first composition comprising a component selected from the group consisting of at least one polymeric material, at least one polymeric precursor, and at least one monomer, and mixtures thereof, to deposit the component on the wafer and form a coating thereon; then

10 (b) imagewise exposing the coating to radiation such that exposed and unexposed coating portions are formed; then

(c) subjecting the coating to a second composition comprising carbon dioxide such that either one of the exposed or the unexposed coating portions are removed from the at least one wafer and the other coating portion is developed and remains on the coating to form an image thereon; then

15 (d) depositing a metal-containing material or an ionic material on the surface of the wafer from which the exposed or the unexposed coating portions are removed; and then

20 (e) removing the exposed or unexposed coating portion from the wafer;

wherein said steps (a) through (e) are performed in the IMPD without the at least one wafer being removed from the IMPD.

35. The process according to Claim 34, wherein said step (a) comprises depositing the component on the wafer using a chemical vapor deposition (CVD) method.

5 36. The process according to Claim 34, wherein the first composition comprises (1) carbon dioxide or (2) carbon dioxide and a co-solvent mixture.

10 37. The process according to Claim 34, wherein said steps (a) through (e) are repeated at least once without removing the at least one wafer from the IMPD.

15 38. The process according to Claim 34, wherein an intermediate layer is present between the coating portion and the substrate, and said process further comprising the step of selectively etching the intermediate layer using the developed coating portion as an etching mask.

20 39. The process according to Claim 38, wherein said step of selectively etching the intermediate layer comprises contacting the intermediate layer with a gas selected from the group consisting of oxygen, chlorine, fluorine, and mixtures thereof.

25 40. The process according to Claim 34, wherein the exposed coating portion has a lower solubility in carbon dioxide relative to the unexposed coating portions, and wherein said step of subjecting the coating to a second composition comprising carbon dioxide comprises removing the unexposed coating portion from the substrate such that the exposed coating portion remains.

30 41. The process according to Claim 34, wherein the polymeric material comprises a fluoropolymer.

42. The process according to Claim 41, wherein the fluoropolymer is formed from monomers selected from the group consisting of fluoroacrylate monomers, fluorostyrene monomers, fluoroalkylene oxide monomers, fluorolefin monomers, fluorinated alkyl vinyl ether monomers, cyclic fluorinated monomers, and mixtures thereof.

43. The process according to Claim 42, wherein the monomers are selected from the group consisting of 2-(N-ethylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-ethylperfluorooctane- sulfonamido) ethyl methacrylate, 2-(N-methylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-methylperfluorooctane- sulfonamido) ethyl methacrylate, 1,1'-dihydroperfluorooctyl acrylate, 1,1'-dihydroperfluorooctyl methacrylate, 1,1',2,2'-tetrahydroperfluoroalkylacrylate, 1,1',2,2'-tetrahydroperfluoroalkyl-methacrylate, α -fluorostyrene, 2,4,6-trifluoromethylstyrene, hexafluoropropylene oxide, perfluorocyclohexane oxide, tetrafluoroethylene, vinylidene fluoride, chlorotrifluoroethylene, perfluoro(propyl vinyl ether), perfluoro(methyl vinyl ether), 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole, and mixtures thereof.

44. The process according to Claim 34, wherein the polymeric material comprises a silicon-containing polymer.

45. The process according to Claim 44, wherein the silicon-containing polymer comprises at least one segment selected from the group consisting of an alkyl siloxane, a fluoroalkyl siloxane, a chloroalkyl siloxane, and mixtures thereof.

46. The process according to Claim 34, wherein the metal-containing material comprises at least one metal selected from the group consisting of aluminum, copper, gold, titanium, tantalum, tungsten, molybdenum, silver, and alloys thereof.

47. The process according to Claim 34, wherein the ionic material is selected from the group consisting of boron, phosphorous, arsenic, and combinations thereof.

5 48. The process according to Claim 34, wherein the radiation is selected from the group consisting of visible, ultraviolet, x-ray, and e-beam.

49. The process according to Claim 48, wherein the radiation is ultraviolet or x-ray and the polymeric material comprises a photo acid
10 generator.

50. The process according to Claim 34, wherein said step of removing the exposed coating portion from the substrate comprises contacting the exposed coating portion with a carbon dioxide containing fluid
15 such that the exposed coating portion is removed from the substrate.

51. The process according to Claim 50, wherein said step of contacting the substrate with a first composition comprising carbon dioxide and a component comprises coating the component using a method selected
20 from the group consisting of a spin coating method, a dip coating method, a meniscus coating method, a coating method using self-assembled monolayers, and a spray coating method.

52. The process according to Claim 34, wherein the polymeric
25 material is a copolymer of 11'-dihydroperfluorooctyl methacrylate and t-butyl methacrylate.

53. The process according to Claim 34, wherein the exposed coating portion has a higher solubility in carbon dioxide relative to the
30 unexposed coating portions, and wherein said step of subjecting the coating to a second composition comprising carbon dioxide comprises removing the

exposed coating portion from the substrate such that the unexposed coating portion remains.

54. The process according to Claim 53, wherein the polymeric
5 material comprises a fluoropolymer.

55. The process according to Claim 54, wherein the fluoropolymer
is formed from monomers selected from the group consisting of fluoroacrylate
monomers, fluorostyrene monomers, fluoroalkylene oxide monomers,
10 fluorolefin monomers, fluorinated alkyl vinyl ether monomers, cyclic
fluorinated monomers, and mixtures thereof.

56. The process according to Claim 55, wherein the monomers are
selected from the group consisting of 2-(N-ethylperfluorooctane- sulfonamido)
15 ethyl acrylate, 2-(N-ethylperfluorooctane- sulfonamido) ethyl methacrylate, 2-
(N-methylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-
methylperfluorooctane- sulfonamido) ethyl methacrylate, 1,1'-
dihydroperefluorooctyl acrylate, 1,1'-dihydroperefluorooctyl methacrylate,
1,1',2,2'-tetrahydroperefluoroalkylacrylate, 1,1',2,2'-tetrahydroperefluoroalkyl-
20 methacrylate, α -fluorostyrene, 2,4,6-trifluoromethylstyrene,
hexafluoropropylene oxide, perfluorocyclohexane oxide, tetrafluoroethylene,
vinylidene fluoride, chlorotrifluoroethylene, perfluoro(propyl vinyl ether),
perfluoro(methyl vinyl ether), 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole,
and mixtures thereof.

57. The process according to Claim 53, wherein the polymeric
25 material comprises a silicon-containing polymer.

58. The process according to Claim 57, wherein the silicon-containing polymer comprises at least one segment selected from the group consisting of an alkyl siloxane, a fluoroalkyl siloxane, a chloroalkyl siloxane, and mixtures thereof.

59. The process according to Claim 53, wherein the metal-containing material comprises at least one metal selected from the group consisting of aluminum, copper, gold, titanium, tantalum, tungsten, molybdenum, silver, and alloys thereof.

60. The process according to Claim 53, wherein radiation is selected from the group consisting of visible, ultraviolet, X-ray, and e-beam.

61. The process according to Claim 53, wherein radiation is ultraviolet or e-beam and the polymeric material comprises a photo acid generator.

62. The process according to Claim 53, wherein said step of removing the unexposed coating portion from the substrate comprises contacting the unexposed coating portion with a carbon dioxide containing fluid such that the unexposed coating portion is removed from the substrate.

63. The process according to Claim 62, wherein said step of contacting the substrate with a first composition comprising carbon dioxide and a component comprises coating the component using a method selected from the group consisting of a spin coating method, a dip coating method, a meniscus coating method, and a spray coating method.

64. The process according to Claim 53, wherein the carbon dioxide soluble polymeric material is selected from the group consisting of a copolymer of a fluoroacrylate and a component selected from the group

consisting of $C(CH_2OH)_3$, a sugar unit, SiR_3 wherein R is a polar group selected from the group consisting of:

5 65. The method according to Claim 34, wherein the composition further comprises a co-solvent.

10 66. The method according to Claim 34, further comprising the step of selectively etching the wafer, wherein said step of selectively etching the wafer occurs subsequent to step (c) but prior to step (d).

15 67. A process of forming integrated circuits comprising the steps of:
(a) inserting at least one wafer into an integrated microelectronics process device (IMPD); then

(b) contacting the at least one wafer with a first composition
20 comprising a component selected from the group consisting of at least one polymeric material, at least one polymeric precursor, and at least one monomer, and mixtures thereof, to deposit the component on the substrate and form a coating thereon; then

(c) imagewise exposing the coating to radiation such that exposed
25 and unexposed coating portions are formed; then

(d) subjecting the coating to a second composition comprising
carbon dioxide such that either one of the exposed or the unexposed coating portions are removed from the at least one wafer and the other coating portion is developed and remains on the coating to form an image thereon; then

30 (e) depositing a metal-containing material or an ionic material on the surface of the wafer from which the exposed or the unexposed coating portions are removed; then

(f) removing the exposed or unexposed coating portion from the substrate; and then

(g) removing the at least one wafer from the IMPD;
wherein said steps (a) through (f) are performed in an IMPD without the at least one wafer being removed from the IMPD.